# Basic Thermodynamics

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## I. Thermodynamic Pressure

Rudolf Clausius invented entropy by considering the change of internal energy as

(1.1) $dU = TdS - pdV$

One might ask, why invent a new variable when we already have temperature?
When we change volume by compression, temperature will change even without heat contact.
We therefore need a new variable that accounts for pure heat flow independently.
The equation has a very precise original meaning: it consider an enclosed object subject to heat contact at its surface: that is what TdS stands for, only!
The object can be compressed against its internal pressure, this is -pdV
As it stands, the equation has too many unknowns. Not only is entropy still to be determined, but the pressure, too, is undefined.
That is not to say that they are experimentally inaccessible: a pressure gauge readily gives a reading and dividing some heat energy by the temperature gives us the entropy change.

The problem is that we have trouble connecting a statistical description with phenomenology.
In statistical mechanics, one assumes that a body is made up of a great number of sub-ensembles which follows some probability law. The subensembles go down to single atoms.
For them, one assumes a Boltzmann distribution

(1.2) $$\varrho_i = \frac{1}{Z}\exp\left(\frac{-1}{T}(\varepsilon_i - \mu N_i)\right)$$

A first step was taken by von Neumann by looking at the entropy equation

(1.3) $dS = (1/T)dU + (p/T)dV$

Instead of looking at a volume change, one looks at a change of particle density to connect with the Boltzmann distribution.

(1.4) $dS = (1/T)dU - (\mu/T)dN$

This equation can be read as: if S is at an extremum with the conditions of given mean energy U and mean density (particle number) N, then the differential of S is connected to said means by Lagrange parameters.
If, additionally, we want the Boltzmann distribution to give said extremal entropy, the latter is given by

(1.5) $$S = -\langle \ln \hat{\varrho} \rangle = \frac{1}{T}\langle U \rangle - \frac{\mu}{T}\langle N \rangle + \ln Z$$

where the bracket means the statistical average. This is the statistical operator averaging itself.

The quantity $\mu N$ is identified as the Gibbs potential.
This identifies the pressure term as

(1.6) $pV = T \ln Z$

## II. Magnetic Energy

Let us now look at a system that does not involve particle densities such as a crystal. As a second variable, we choose its magnetisation M in an external field $H_{ex}$.
Why a second variable? Because fun starts at two. With only one variable, there is no need to introduce any coefficient function. It's a purely mathematical affair.

(2.1) $dU = TdS + H_{ex}\, dM$

Here we have our first problem: energy is not conserved anymore!
In principle, we are allowed to change magnetisation, which is a volume quantity proper to our object, thermally isolated (dS = 0) and change energy: the object can change its own energy by itself!

Let's form the magnetic enthalpy

(2.2) $J = U - MH_{ex}$

(2.3) $dJ = TdS - MdH_{ex}$

This makes much more sense.
Now, J is changed by external quantities only. Let us not forget that TdS is heat contact through a surface.

Let us go back to entropy

(2.4) $dS = (1/T)dU - (H_{ex}/T)dM$

We are in the same situation as in chapter I except that magnetisation has taken the spot of particle numbers.
The Boltzmann distribution now reads

(2.5) $$\varrho_i = \frac{1}{Z}\exp\left(\frac{-1}{T}\left(\varepsilon_i - H_{ex} M_i\right)\right) = \frac{1}{Z}\exp\left(\frac{-1}{T} J_i\right)$$

which gives entropy

(2.6) $$S = -\langle \ln \hat{\varrho} \rangle = \frac{1}{T} J + \ln Z$$

Magnetic enthalpy has taken the role of energy.
The Gibbs potential becomes

(2.7) $$G = J - TS = -T \ln Z$$

which is always negative (!) and quite a change from chapter I. where (T ln Z) had a completely different meaning.